

Accurate numerical approach to Quantum Mechanics

Miquel Bosch, Guillem Megías and Gerard Pascual

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Quantum Mechanics is considered as one of the most weird branches in physics with the most, although accurate, counterintuitive predictions. The problem lies not on the theory but on what it is trying to explain: the microscopic world. Moreover, due to the complicated form of the Schrödinger equation, there are only few examples where an analytical solution to the problem exists. Therefore, the motivation of this paper is to explore the effects of Quantum Mechanics solving the Schrödinger equation numerically for different potentials. Firstly, the algorithms and the numerical methods used to calculate the eigenvalues and the eigenstates are explained. Subsequently, on the results section, the numerical system is stressed to find out its precision and the method is used for two real models: the ammonia molecule and the hydrogen atom. Finally, an applet that uses the numerical system of this paper is discussed.

I. INTRODUCTION

The aim of the paper is to solve numerically the Schrödinger equation for any arbitrary potential under certain boundary conditions. As we are interested on the position representation of the state, all the systems and equations will be given on the position basis. Generally, the Schrödinger equation is a partial differential equation but, when it only depends on one variable, it becomes an ordinary differential equation (ODE). Furthermore, if the potential does not depend explicitly on time (i.e. conservative system), the Schrödinger equation turns into an eigenvalue problem. The first and easiest case that will be analyzed is the one-dimensional problem. The Schrödinger equation in one-dimensional and in the position basis it can be expressed as follows,

$$-\frac{\hbar^2}{2m} \frac{d^2\phi(x)}{dx^2} + V(x)\phi(x) = E\phi(x), \quad (1)$$

where \hbar is the reduced Planck constant, m is the mass of the particle, $V(x)$ is the potential, E is the energy and $\phi(x)$ is the eigenstate. The boundary conditions imposed are $\phi(x_{min}) = 0$ and $\phi(x_{max}) = 0$ as we are looking for bound states.

Another case where the Schrödinger equation becomes an ordinary differential equation is in the case of a three-dimensional problem with a decoupled potential. The eigenstates can be written in the following way,

$$\psi(\mathbf{r}) = \frac{\phi(r)}{r} Y_{lm}(\theta, \varphi), \quad (2)$$

where $\phi(r)$ must satisfy equation 1 changing x for r and adding to the potential the centrifugal barrier,

$$V_l(r) = V(r) + \frac{\hbar^2}{2m} \frac{l(l+1)}{r^2}. \quad (3)$$

Here the boundary conditions imposed are that $\phi(0) = 0$ and $\phi(r_{max}) = 0$.

II. NUMERICAL METHODS

To solve numerically the ODE, first it must be discretized using a step size, $h = (x_{max} - x_{min})/N_{interv}$, where N_{interv} is the number of intervals. The second derivative then becomes, $-d^2\phi(x)/dx^2 \rightarrow -(\phi(x-h) + 2\phi(x) - \phi(x+h))/h^2$. By discretizing the ODE, the problem is reduced to find the eigenvalues and eigenstates of the resulting matrix,

$$\begin{bmatrix} d_1 & e_1 & 0 & 0 & \dots & 0 & 0 \\ e_1 & d_2 & e_2 & 0 & \dots & 0 & 0 \\ 0 & e_2 & d_3 & e_3 & \dots & 0 & 0 \\ \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots \\ 0 & 0 & 0 & 0 & \dots & d_{n-1} & e_{n-1} \\ 0 & 0 & 0 & 0 & \dots & e_{n-1} & d_n \end{bmatrix} \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \vdots \\ \phi_{n-1} \\ \phi_n \end{bmatrix} = E \begin{bmatrix} \phi_1 \\ \phi_2 \\ \phi_3 \\ \vdots \\ \phi_{n-1} \\ \phi_n \end{bmatrix}$$

where $n = N_{interv} - 1$, $d_k = \frac{2}{h^2} + V_k$ and $e_k = -\frac{1}{h^2}$. For simplicity's sake, it has been considered the Planck constant and the mass equal to 1.

A. Eigenvalues

Once the ODE has been discretized, the eigenvalues (i.e. the energy levels) of the system can be found. When the matrix has this particular shape, called tridiagonal, several efficient algorithms exist to find the eigenvalues.

In this paper, Sturm's method was used. This method is based on Sturm's theorem that relates the number of eigenvalues smaller than a given value with the change in sign of a recursive sequence of polynomials called Sturm sequence [4]. The algorithm first calculates the upper and lower bounds of the eigenvalues. Since Sturm's Theorem states that when the polynomials are evaluated for a specific value, the number of changes in sign indicates the number of eigenvalues smaller than the given value, the precise value where the number of smaller eigenvalues changes can be found by bisection, and thus the eigenvalue is found [4]. If for a given value, one of the polynomials is equal to zero, then it is considered as a change in

sign and the algorithm jumps the following polynomial to the next one. When the tolerance limit is achieved, the code breaks the infinite loop and gives the results obtained.¹

The algorithm explained above, as it can be seen in section III A, gives an accurate result after few iterations for $N_{interv} = 1000$ (three decimals of precision). However, the limit of this numerical method is that the eigenvalues found are from the discretized matrix and not from the ODE. Knowing that the error between the discretization and the continuous equation goes as a polynomial series of h^2 , this algorithm can easily be improved using the extrapolation of Richardson that extrapolates the eigenvalues for $h = 0$. As it is showed below, this extrapolation improves dramatically the value of the energy.

B. Eigenstates

To calculate the eigenstates, the discretization matrix can be easily solved as it has a tridiagonal shape. Furthermore, as the Schrödinger equation is linear, the first value of the eigenfunctions ϕ_n can be arbitrarily chosen. However, two considerations have to be taken into account: the appearance of overflow due to the exponential growth of wavefunctions and the rounding error when they decrease exponentially. For these two reasons, the integration is performed in two different intervals and then, they are joint imposing continuity. Finally, wavefunctions are conveniently normalized.

III. RESULTS

A. Precision of the algorithm

The numerical method developed has been widely tested in the modified Pöschl-Teller potential in 1-D, which is very steep and useful to prove precisely the robustness of the algorithm. It also admits an exact analytical solution, thus allowing to figure out the precision of the developed numerical method. The expression of the potential is, in dimensionless coordinates:

$$V(x) = -\frac{\lambda(\lambda-1)}{\cosh^2 x}. \quad (4)$$

The minimum of the potential is located at $x = 0$ and its depth is $\lambda(\lambda-1)$. The exact eigenvalues and the odd and

even eigenfunctions extracted from [2] are the following:

$$E_n = -\left(\sqrt{\lambda(\lambda-1)} + \frac{1}{4} - \left(n + \frac{1}{2}\right)\right)^2,$$

$$u_e(x) = \cosh^\lambda x {}_2F_1\left(a, b, \frac{1}{2}; -\sinh^2 x\right),$$

$$u_o(x) = \cosh^\lambda x \sinh x {}_2F_1\left(a + \frac{1}{2}, b + \frac{1}{2}, \frac{3}{2}; -\sinh^2 x\right).$$

These energies are integer numbers when $\lambda \in \mathbb{N}$ and $\lambda > 1$. It should also be noticed that the eigenfunctions depend on the hypergeometric function ${}_2F_1$.

The tridiagonal algorithm by itself shows a clear convergence in the following table when $\lambda = 6$, when the exact values are $E_0 = -25$, $E_1 = -16$, $E_2 = -9$, $E_3 = -4$.

N	E_0	E_1	E_2	E_3
100	-25.01389972	-16.05150669	-9.08896123	-4.09647595
200	-25.00346377	-16.01279929	-9.02201760	-4.02373068
500	-25.00055371	-16.00204447	-9.00351304	-4.00377439
1000	-25.00013841	-16.00051100	-9.00087791	-4.00093782
2000	-25.00003460	-16.00012774	-9.00021945	-4.00022923
5000	-25.00000554	-16.00002044	-9.00003511	-4.00003087

TABLE I Energies of the bound states for different N using the tridiagonal algorithm.

It is easily observed that with $N = 10^3$, the errors are smaller than 10^{-3} , and precision can increase even more if N is raised. However, Richardson's extrapolation can yield to much more precise results. In Table II the values are compared, again with $\lambda = 6$.

Exact result	Tridiagonal N = 1000	Richardson
-25	-25.00013841	-25.00000000
-16	-16.00051100	-15.99999999
-9	-9.00087791	-8.999999970
-4	-4.000937820	-3.999993040

TABLE II Comparative of the obtained energies of the bound states with each algorithm.

Richardson's extrapolation yields to much more precise results, ensuring errors lower than 10^{-8} for the ground state. Energy levels near to zero are numerically bad conditioned and cannot have the same exactness, but still errors are lower than 10^{-5} .

Wavefunctions are also easily calculated with the algorithm and the exactness is still satisfactory. The difference between the analytical solution and the numerical approach is shown in Figure 1.

¹ The programming language used in this paper is PYTHON.

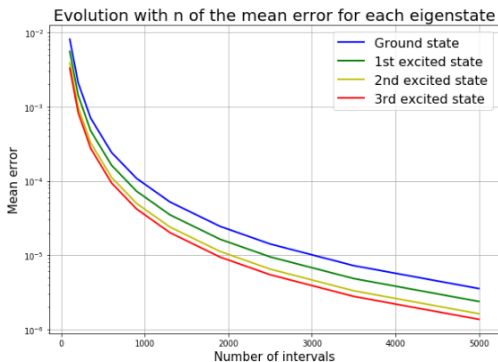


FIG. 1 The mean difference between analytical and numerical solutions. The algorithm is robust as this error decreases with increasing N

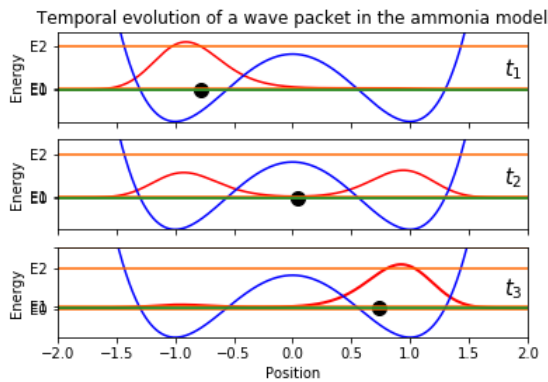


FIG. 2 Different frames ($t_3 > t_2 > t_1$) of the temporal evolution of a wave packet composed of $\psi(x) = \frac{2}{\sqrt{53}}(3\psi_0 + 2\psi_1 + 0.25\psi_2)$. The orange lines and the green line represent the energy levels and the average energy respectively. The red line shows the probability density and the black dot shows the average position. The double well potential is represented as the blue line.

B. Examples of real models

1. Ammonia molecule

The ammonia molecule (NH_3) is composed of three hydrogen atoms that form the base of a pyramid with a nitrogen atom in its apex. Although the hydrogen atoms create a potential barrier, the nitrogen can tunnel them and it can be found in both sides of the base of the pyramid. A simple model that can describe this problem is the double well potential ($V(x) = \alpha(x^2 - 1)^2$). Using the numerical methods described above, the first eigenvalues and eigenstates were found and since they are stationary states, the temporal evolution of a wave packet can easily be calculated. In figure III B 1 different frames from the probability density evolution of a wave packet in the

ammonia molecule potential are shown.²

It can be seen how the peak of the probability density moves from one well to the other showing the possibility that the nitrogen atom can be in both sides of the pyramid. This behavior fits correctly with the approximated analytical solutions [1].

2. Hydrogen atom

As mentioned previously in section I, the three-dimensional problem analogy can be solved similarly. A well-renowned example of this case is the Hydrogen atom. Therefore, the aim of this simulation section was to numerically obtain the different components of the wave-function of the Hydrogen atom; computing and representing, thereafter, the probability density function of both terms of the wave-function.

As for the radial component of the wave-function, $R_{nl}(r) = \frac{\phi(r)}{r}$, the equation 3 must be solved with a certain l azimuthal quantum number. Using the numerical methods presented earlier, this ODE was solved for different l values.

From the radial eigenstate, the radial probability density function can be computed as the probability of finding an electron in the volume enclosed by two spheres of a radii difference of dr , that is,

$$P_{nl}(r) = 4\pi r^2 R_{nl}^*(r) R_{nl}(r), \quad (5)$$

where n is the number of the radial eigenstate and l the azimuthal quantum number. In Figure 3 it is shown the probability density that we have obtained.

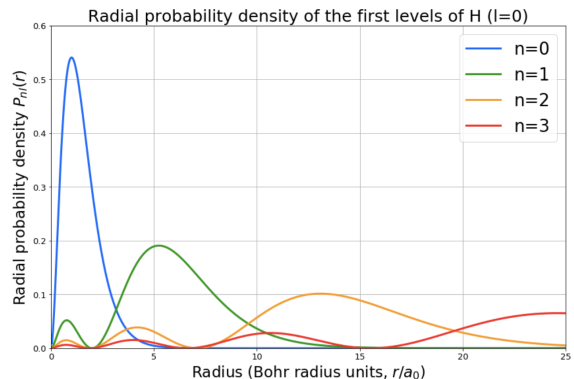


FIG. 3 Radial probability density function P_{nl} of the four first energy levels of the Hydrogen atom for the azimuthal quantum number $l = 0$, already normalized.

Finally, to completely describe the wave-function of the H atom, $Y_{lm}(\theta, \varphi)$ has to be obtained. It can be

² The whole simulation can be seen in the following link: https://www.youtube.com/watch?v=m3_smsdw8Kk

shown that this angular component can also be decoupled, $Y_{lm}(\theta, \varphi) = \Phi(\varphi)\Theta(\theta)$; where both components satisfy different differential equations, which can be solved analytically. Finally, the angular solution yields,

$$Y_{lm}(\theta, \varphi) = (-1)^m \sqrt{\frac{(2l+1)(l-m)!}{4\pi(l+m)!}} P_{lm}(\cos\theta) e^{im\varphi},$$

where $P_{lm}(\cos\theta)$ is the associated Legendre polynomial. From this last equation, the angular probability density can be obtained.

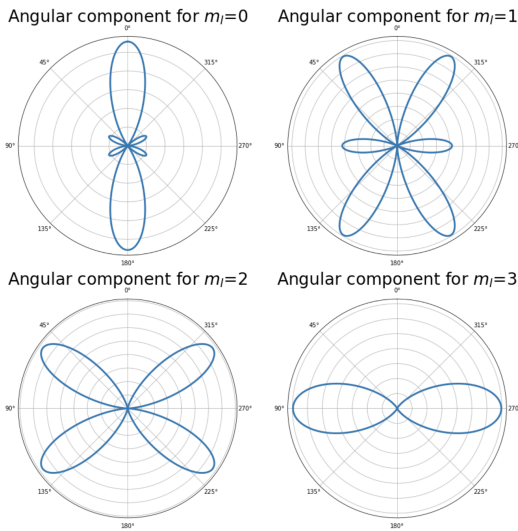


FIG. 4 Polar representation of the angular probability density for the different magnetic quantum numbers m_l associated to $l = 3$. The 0° axis corresponds to the z-axis.

In Figure 4 a polar representation of this probability density for the different m_l , associated to $l = 3$, are presented. It should be highlighted that this probability density just depends on θ and does not depend on ϕ . Therefore, it can also be represented readily, for both angles, in 3D. In Figure 5 the different 3D angular probability density functions for $l = 3$ are presented.

Physically, this angular probability density representation gives a clear idea on how electron orbitals look like in reality, since it gives the probability for an electron of being in a certain point in space. Nevertheless, a complete wave-function representation would necessarily include the radial component altogether with the angular one. Still, this would lead to a rather complicated representation.

IV. DISCUSSION AND CONCLUSIONS

In conclusion, the developed numerical approach for solving the Schrödinger equation for different given potentials has been shown to give a rather accurate, robust and computationally rapid results, whose precision has

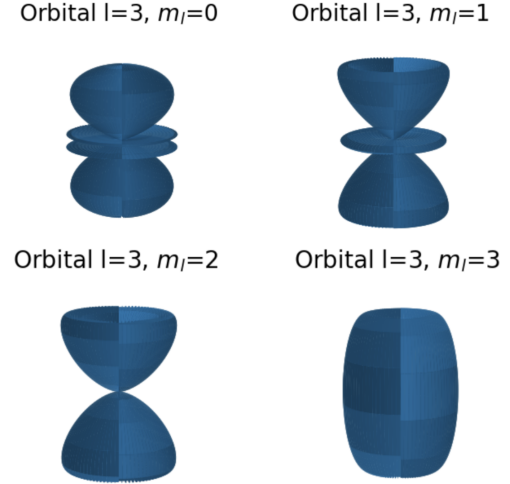


FIG. 5 3D representation of the angular probability density for the different m_l corresponding to $l = 3$.

been corroborated in different cases and, in particular, for the modified *Pöschl-Teller* potential.

This method allows solving much more examples than just analytically, which highlights the importance of a numerical approach in quantum mechanics. In this sense, the ammonia particle analogy with the double-well potential and the hydrogen atom three-dimensional probability density functions -giving a first intuition for the orbital shape of the electron- showed also the applicability and interest of the numerical programs and representations developed.

Furthermore, to ease the study and research which such potentials, this numerical approach has been presented in a user-friendly context, using **Python Jupyter notebook**, from which the user can obtain eigenvalues, eigenstates and an animation of the temporal evolution of the probability density of a particle for the certain potential introduced into the applet³.

V. ACKNOWLEDGEMENTS

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- [1] B. Diu C. Cohen-Tannoudji and F. Lalœ. *Quantum Mechanics V1*. Wiley-vch, 1977.
- [2] S. Flügge. *Practical Quantum Mechanics*. Springer-Verlag Berlin Heidelberg, 1999.
- [3] R. Resnick R. Eisberg. *QUANTUM PHYSICS of atoms, molecules, solids, nuclei and particles*. John Wiley, 1985.
- [4] Emili Higón Rafael Guardiola and Josep Ros. *Mètodes nummèrics per a la física*. Universitat de València, 1995.

³ The PYTHON program can be accessed online: <https://gmegh.>